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Analysis of engineered opals for photonic band gap properties at visible wavelengths

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Abstract : We have performed calculations using a modified Transfer Matrix method to study the photonic band gap properties of bare opals of different diameters, different number of layers, sintered opals with filling fractions varying between 0.74 and 1.00, partial and complete coating with semi-conducting GaN and lastly, inverted opals. The two prominent directions of [001] and [111] have been analyzed. Sintering improves the pseudo-gap and shifts the energy range of its occurrence, while partial coating gives a larger fall in transmission coefficient than complete coating. Inverted opals in GaN background show a stop band with lower transmission coefficient compared to coated opals due to an improvement in dielectric contrast. Our computational approach with the modified transfer matrix method based on a cubic unit cell in spherical polar coordinates is easier to implement with comparable accuracy as other methods to study electromagnetic wave propagation in different directions.

Keywords Photonic crystals, opals, sintering, transfer matrix method

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1. Introduction

It is now well established that periodic dielectric structures, called photonic crystals, have the ability to control the propagation of electromagnetic waves. These photonic crystals exhibit frequency ranges or photonic band gaps where the electromagnetic waves cannot propagate. This range is governed by the periodicity of the structure. The early suggestions of inhibition of spontaneous emission [1] and localization of light [2] with photonic crystals still continue to be the motivation for current studies. The presence of a photonic band gap in the visible range can have profound impact on the efficiency of several optical devices including LEDs, lasers and optical switches [3,4]. Photonic band gap at visible wavelengths requires a dielectric constant periodicity in the nanometer scale. Self-assembled systems, such as synthetic opals, hold a lot of promise for applications at visible wavelengths [5-7].

Bare synthetic opals consisting of nano-size SiO_2 spheres, under carefully controlled chemical conditions, self-organize themselves in a close-packed *fcc* structure [8-11] and have a pseudo-gap in the range of visible wavelengths [12]. A variation in the diameter of these spheres, with values such as 250 nm, 210 nm and 160 nm, gives a different color to the sample such as red, green and purple respectively due to the position of the stop band in transmission. It is known that the photonic gap can be improved in terms of its mid-gap frequency, width etc, by increasing the filling fraction (sintering) and by in-filling the silica voids with materials of higher dielectric constant (such as by coating and etching for inversion) [12].

In this work, we present a systematic computational study of opal-based photonic crystals. A modified version of Transfer Matrix Method (TMM) [13, 14] has been used to study the transmission coefficient (T) of these structures. Parameters such as variation in sample thickness, sintering, coating and inversion have been analyzed through these calculations for further improvement of the photonic band gap properties.

2. Present studies

2.1 Computational approach :

This work uses the TMM since it has the advantage of calculating the transmission and reflection coefficients for

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incident electromagnetic waves on a finite slab of photonic crystal, in addition to the band structure. It is also useful when the dielectric constant is complex or frequency-dependent. The transfer matrix calculates the electric and magnetic fields in a plane, given the respective fields in the previous plane. The method uses the equivalence of Bloch boundary conditions to calculate the k values for a given energy (frequency) range.

The original code in [14] had been written for a simple-cubic unit cell in rectangular coordinates specifically for electromagnetic wave propagation in [001] direction. We have modified the code extensively to incorporate a *fcc* unit cell as well as to study other directions of propagation. By the use of spherical polar coordinates, propagation along [111] direction is easily studied. By changing the radial and azimuthal angles, any direction of propagation can be analyzed. This is easier to implement than the TMM approach used in [15] where different unit cells should be defined for propagation along directions other than [001] and a prismatic unit cell was used for [111] direction. The computational accuracy is thus assured to be the same for any direction of electromagnetic wave propagation in our approach. A grid of 15 × 15 × 15 has been used inside the cubic unit cell for good convergence in all our calculations. Unlike the calculations based on plane wave method and finite-difference time domain method which require enormous computer time and memory, these calculations can be done on a DEC-Alpha work-station. Even though it is possible to calculate both the band structure and the transmission coefficient by this method, we have shown only the variation of transmission coefficient with energy since the direction of propagation is fixed to be either [001] or [111] instead of a band structure diagram for the entire Brillouin zone.

2.2 *Bare synthetic opal*

A complete photonic band gap will suppress propagation of the electromagnetic waves in all the directions of the first Brillouin zone. Bare opals do not exhibit a complete band gap since the refractive index contrast between silica and air (1.5:1.0) is small. In the case of bare opal, the gap energy can be tuned by varying the diameter of the silica spheres. The sphere sizes of 250 nm, 210 nm and 160 nm are referred to as red, green and purple opal respectively. The possibility of tuning the mid-gap energy for any specific application is a very attractive feature of these materials. By varying the sample thickness, at any given sphere size, one can obtain a better gap in the two most important directions of propagation, namely [001] and [111]. When the thickness is increased from 8 layers to 128 layers, the transmission coefficient at mid-gap falls to lower values and the mid-gap energy shifts to higher values. This is another way of tuning the stop band energy and the results in Figure 1 are those of red opal with sphere diameter of 250 nm in [001] direction. The mid-gap value of transmission coefficient (T_{min}) falls exponentially with increase in crystal thickness. The reciprocal of the slope of the plot of log (T_{min}) against the sample thickness (in terms of a) gives the attenuation length equal to 68 a, where a is the lattice constant of the structure. Reynolds *et al.* [15] obtained 87.4a for the attenuation length. The level of accuracy is not expected to be the same in the two methods and hence this discrepancy is within tolerable limits. The filling fraction is 0.74 for the results in Figure 1. Similar results are obtained for green and purple opals in the [001] direction. From the band structure of opal [15], the gap for red opal along [001] direction is expected near 2.5 eV, as obtained in our calculations.

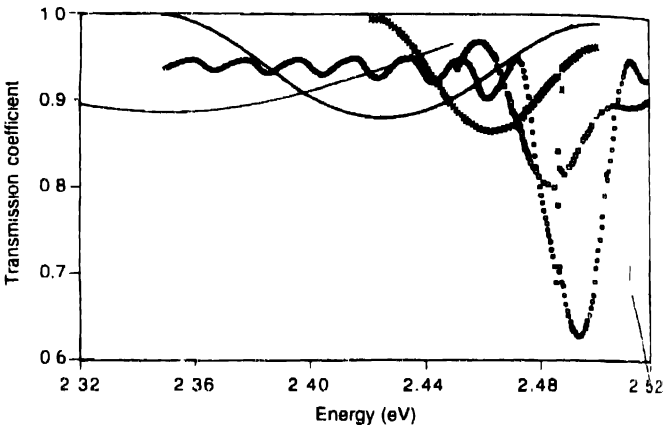

Figure 1. Transmission studied along [100] for red opal of different thickness. Thin solid line : 8a, thick solid line : 16a, crosses : 32a, squares : 64a and circles : 128a.

For propagation along [111] direction, Reynolds [16] employed a prismatic unit cell with 7 × 13 × 18 grid points. In our approach, spherical polar coordinates with a cubic unit cell and the radial and azimuth angles at 45^0 each has been used to study the [111] direction. The presence of the gap for different number of layers, varying from one to 8 layers, can be seen in Figure 2. The most noticeable difference is in the fall in transmission coefficient with an increase in thickness, even within a few layers. This is more rapid in the [111] direction and the attenuation length is much lesser, about 5 a. In comparison,

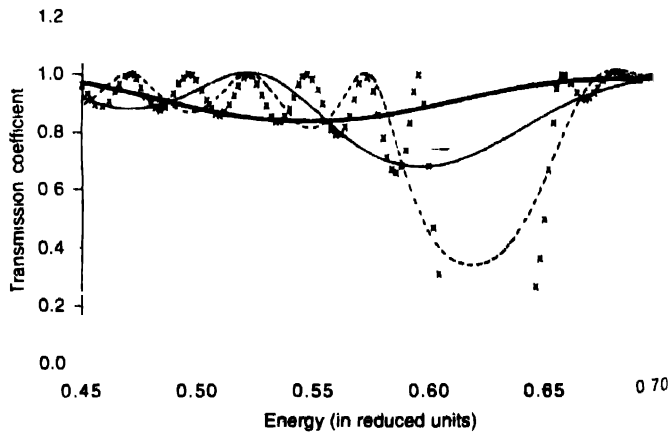

Figure 2. Transmission coefficient along [111] for red opal of different thickness. Thick solid line : a, thin solid line : 2a, dotted line : 4a and crosses : 8a

the attenuation length reported by Reynolds *et al.* [15] was $3.44a$. The [111] direction gives a better band gap with fewer layers.

As mentioned earlier, a change in the sphere diameter (at a fixed fill fraction) leads to a shift of the band gap. In order to illustrate this, the energy may be represented in reduced units of $\omega a / 2\pi c$ as in Figure 2. The absolute energy values for any sample of opal may be obtained by the use of its lattice constant (which is in turn known from the sphere diameter of silica at close-packing filling fraction).

2.3 Sintered opal :

Synthetic opals have a low mechanical strength that can be improved by an annealing process under applied pressure known as sintering [10]. Temperatures up to 950° C do not lead to any significant structural difference. In this region, the filling fraction is 0.74 with the silica spheres just in contact. Above this temperature, the pore volume decreases as the spheres crush into each other. Thus, the sintering process produces an increase of the contact section between the nearest neighbors, making the structure more robust. In addition, the optical properties get modified [17] because of the increase in filling fraction of the spheres due to overlap and the reduction in the lattice constant (final value is a') due to sintering. We have simulated sintering by considering a small reduction in the lattice constant thus allowing an overlap of the spheres. For propagation along both the directions, [001] and [111], we observe a drop in transmission coefficient till the pore size is decreased to 5%. A further reduction in pore size closes the gap since the spatial modulation of dielectric constant is not significant. These results are seen in Figure 3

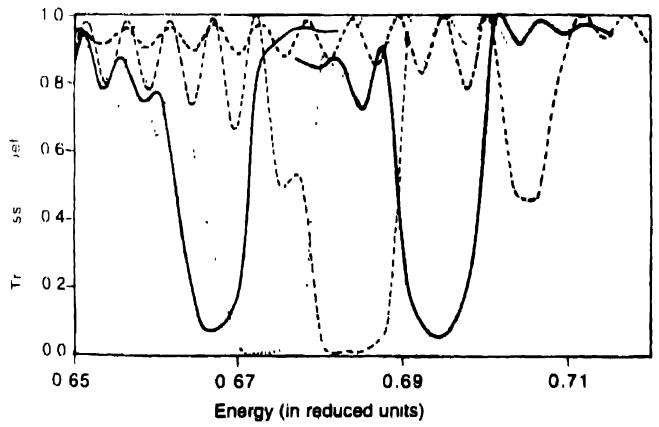

Figure 3. Transmission coefficient as a function of energy (in reduced units of a' / λ) in sintered opal The filling fractions of silica after sintering are 0.80 (thin solid line), 0.85 (dotted line), 0.90 (dashed line), 0.95 (thick solid line) and 0.98 (thick dotted line).

The approximate wavelength corresponding to the transmission minimum can be obtained analytically from the Bragg's law, $\lambda(at\ T_{min}) = 2d\ n_{eff}$. In this expression, d is the separation between the crystal planes for any direction of propagation ($d = a$ in [001] direction and $d = 0.816\ a$ for [111] direction) and n_{eff} is obtained from the fill fractions and the refractive indices of the spheres and the background. However, the expected value of T_{min} can not be found from this simple empirical relation. The energy values estimated from this law and the trends predicted by it match well with our calculated results.

The effect of sintering on the relative width of the gap (given by the ratio of the gap width to the mid-gap frequency) for propagation along [001] and [111] was analyzed. These results concur with those in [15], where they were estimated through plane wave method and finite difference techniques. The gaps in both [001] and [111] directions improve due to sintering. But when the sintering is too large (>95%), most of the voids of opal are removed, it becomes a homogeneous structure, and the gap disappears. Due to sintering, the structure shrinks resulting in a smaller lattice constant. This leads to an increase in mid-gap energy in absolute units.

2.4 Coated opal :

Since bare opals have a porous structure, certain nano-materials can be infiltrated into the void spaces through the coating process [18, 19]. The photonic crystal properties of the bare opals can be thus enhanced by improving the dielectric contrast between the coated material and the silica spheres. It is usually carried out by a chemical process and the infiltrated material inherits the 3-D periodicity of the host [18]. Coating can lead to reduced spontaneous emission for subsequent use in high efficiency lasers, if the coated material, such as a semiconductor, has a high dielectric constant and an emission band matching the stop band of the opal [19,20].

We have analyzed the coating effects of opals with a final filling fraction of 0.74, without any sintering. Coating leads to a shift of the minimum gap energy and a fall in the minimum transmission coefficient. Partial coating gives a wider gap and a larger fall in the transmission coefficient than the completely coated opal. This trend is not obvious from the empirical law mentioned earlier. It is clear that a varied spatial modulation of the dielectric constant, such as in a multi-layer structure gives a better gap. The results in Figure 4 correspond to a bare opal, a partially coated opal and a completely coated opal. The material studied for coating is GaN since its dielectric constant is large, of the order of 8.91. In addition, it does not absorb in the energy range studied. In partial coating, the silica spheres have a filling fraction of 0.65 and GaN has a filling fraction of 0.09, so that there is no sintering effect. In complete coating, the silica spheres have a fill fraction of 0.74 and the coated material (GaN) has a fill fraction of 0.26. The simple Bragg law calculation shows that the effect of coating is to shift the mid-gap frequency to lower values, as seen in Figure 4.

A comparison between the attenuation lengths of bare and completely coated (with GaN) opal shows that the value for the latter case is nearly half of that of the former. Therefore, to reduce transmission by the same amount, the coated opal will require half the number of layers compared to bare opal, indicating their commercial importance. Coating is an elegant method to enhance the utility of these materials and opens a new frontier for opal-based composites. Earlier studies have reported the results on opals infiltrated with organic dyes [21-23] and conducting polymers [24-26]. The luminescence properties of the in-filled materials can be modified through the photonic crystal properties of the host. There is an additional advantage since the characteristics of photo-chromatic dyes and conducting polymers change with temperature and light irradiation. Temperature tuning of the band gap is possible if the in-filled materials have liquid crystal properties [27].

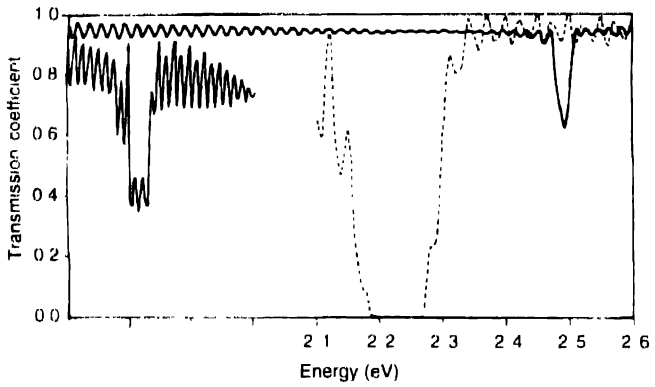

Figure 4. Effect of coating red opal with GaN for propagation along [100]. Thick solid line: bare opal, dashed line: partially coated and thin solid line: completely coated.

2.5 *Inverse opal*

Bare opals can be used as templates to obtain materials called inverse opals [12, 28]. In an inverted opal, the voids of mildly sintered opal are filled with a material of high dielectric constant and the silica spheres are etched out by a chemical route. The formation of larger contact regions during sintering provides channels for the chemically dissolved silica to be removed during etching. The structure is that of a 3D array of sintered nano-size air spheres in a dielectric background. However, infiltration into a close-packed structure is a difficult task and it usually leads to air spheres in a partial dielectric background after chemical etching. For our studies, we have assumed that the bare opal is completely infiltrated with GaN and the silica spheres to be removed completely. So, the structure is that of air spheres in a background of GaN. Figure 5 shows the results for air sphere diameters of 160 nm, 210 nm and 250 nm for propagation in [111] direction. In this figure, the transmission spectra for each sphere size are shown only over a limited energy range for the sake of clarity. Other than the prominent minima shown, there are only smaller minima due to the oscillatory structure in this energy range.

It can be noticed that the transmission coefficient at the mid-gap energy is very small, thus a better gap is obtained, for inverse opal because of the large dielectric contrast (1.0 : 8.9) between the spheres and the background. A comparison with Figure 2 for the bare red opal of the same thickness $8a$ along [111] will illustrate this point very clearly. The inverse opal also gives a narrower gap. The Bragg law calculation for [111] direction yields energies of 2.01 eV, 2.38 eV and 3.13 eV for sphere diameters of 250 nm, 210 nm and 160 nm respectively. These energy values compare very well with those obtained in our calculations, as seen in Figure 5. An improvement in the photonic band gap properties of opals can thus be brought about by appropriate sintering, coating and inversion. Opal-based structures continue to attract a lot of attention from researchers as of date [29].

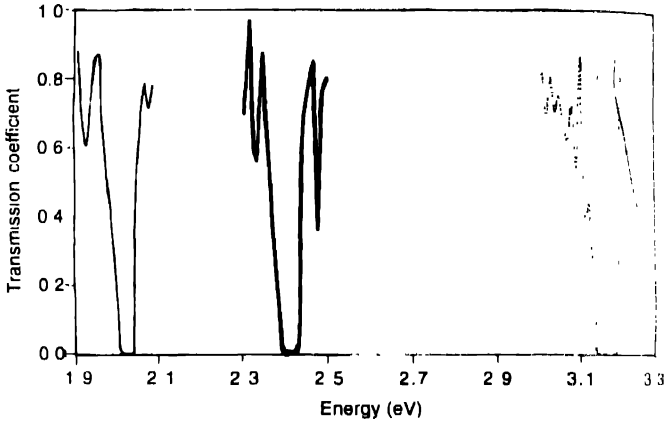

Figure 5. Transmission properties of inverse opal containing air spheres in a dielectric background of GaN. The diameters of the spheres are 250 nm (thin solid line), 210 nm (thick solid line) and 160 nm (thin dashed line).

3. Conclusions

Our computational studies with the modified transfer matrix method based on a cubic unit cell in spherical polar coordinates have enabled us to analyze the electromagnetic wave propagation in [001] and [111] directions for opal-based structures with coating, sintering and inversion. The utility of the method is amply clear since the results are comparable to those published by others using the calculations based on plane wave method and finite-difference time domain method. This method is easier to implement with comparable accuracy and is intuitively easier to understand. The various directions of propagation of the electromagnetic wave can be analyzed by changing the radial and azimuth angles. Compared to the bare opal, the sintered opal has its gap at a higher energy while coating with a material of higher dielectric constant leads to a shift of the gap to lower energies. All the three cases of sintering, coating and inversion give better photonic stop bands in terms of lower values of T_{min}. The simple analytical calculation of the gap energy from Bragg's law is very close to the stop ba energies obtained in our calculations. Inverse opal gives narrower

gaps as required in spectral filtering applications, clearly emphasizing the role of the spatial modulation of refractive index in these materials.

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